THE AMERICAN MINERALOGIST, VOL. 55, MAY-JUNE, 1970

NEW ELECTRON PROBE AND OPTICAL DATA ON GOLD TELLURIDES

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ABSTRACT

Electron probe analysis of sylvanites reveals considerable compositional variations in specimens from different deposits. Gold contents are frequently higher than suggested by the formula $AuAgTe_4$. Spectral reflectivity values increase with increasing gold content. In spite of deviations from stoichiometry, the compositional field of sylvanite is clearly separated from those of krennerite and of calaverite. Nagyagite corresponds to the composition $Pb_{5.00}Au_{0.77}Sb_{1.10}(Te_{2.02}S_{5.43})_{7.45}$ (Cripple Creek) and $Pb_{5.00}Au_{0.66}Sb_{1.06}(Te_{2.23}S_{5.40})_{7.63}$ (Nagyag).

INTRODUCTION

Considerable data on some descriptive aspects of telluride mineralogy and on phase relations in the systems Au-Ag-Te and Ag-Te have accumulated in recent years (Stillwell, 1949; Markham, 1960; Cabri, 1965; Kracek, Ksanda and Cabri, 1966; Terziev, 1966). Kelly and Goddard (1969) published a comprehensive monograph on the telluride ores of Boulder County, Colorado. These have contributed a great deal to our understanding of both, the physical chemistry and the conditions of formation of tellurides. Little, however, is known about compositional variations and spectral reflectivity of these mostly fine-grained ore minerals. The advent of multi-channel electron probes and sophisticated microphotometers in recent years has facilitated the quantitative approach to these problems. Of particular interest is the correlation of optical and compositional parameters. In cases where a well-defined relationship between, say, Au-content and reflectivity does exist, it might be possible to determine deviations from stoichiometry by measurements of spectral reflectivity. The fact that some telluride associations are of value as geological thermometers serves to further stress the significance of correlating electron probe and reflectivity data.

EXPERIMENTAL METHODS

The analyses were performed on an ARL model EMX electron probe microanalyser. The instrument provides facilities for simultaneous determination of three elements. In general, at least 50,000 counts were accumulated for each measurement. This gives a statistical accuracy of better than 1%. Accelerating voltages of 25 kV and specimen currents of 0.3 μA measured on a brass reference surface were used unless otherwise noted. The quantitative data obtained were corrected for background, detector deadtime, absorption, atomic number effect and characteristic fluorescence using the method suggested by Smith (1965). To facilitate the processing of large amounts of data, a FORTRAN program written for the IBM 7094 computer (Rucklidge, 1967) was used. The computer time required to process a nine-element analysis is about 0.6 seconds. Standard deviations are

quoted in the analyses. These estimates of error are based on the quantitative data only, such as the counting statistics and repeated counts on the same specimen. It has not been possible in this study to estimate the errors due to less controllable factors such as specimen preparation, instrumental variations and uncertainties in the correction procedure.

Pure elements as well as synthetic gold and silver tellurides, kindly made available by Dr. L. Cabri, have been used as standards. Details of the synthetic standards are given in Cabri and Rucklidge (1968).

Measurements of spectral reflectivity have been performed using a Zeiss MPM microphotometer. Elba pyrite cut parallel to (111) served as a reflectivity standard; it was calibrated against the pyrite "*b*", measured by the National Physical Laboratory, as quoted by Bowie (1967, p. 125). The spectral reflectivities of the two standards proved virtually identical. Relative errors are in the range of 2 percent of the values measured.

Experimental Results

Sylvanite. High reflectivity and distinct twinning, combined with strong anisotropy and pleochroism, facilitate microscopic determination of sylvanite. The material investigated during the present study includes, amongst others, specimens from Cripple Creek, Colorado, and from the Emperor Mine, Vatukoula, Fiji. Figure 1 illustrates a telluride associa-

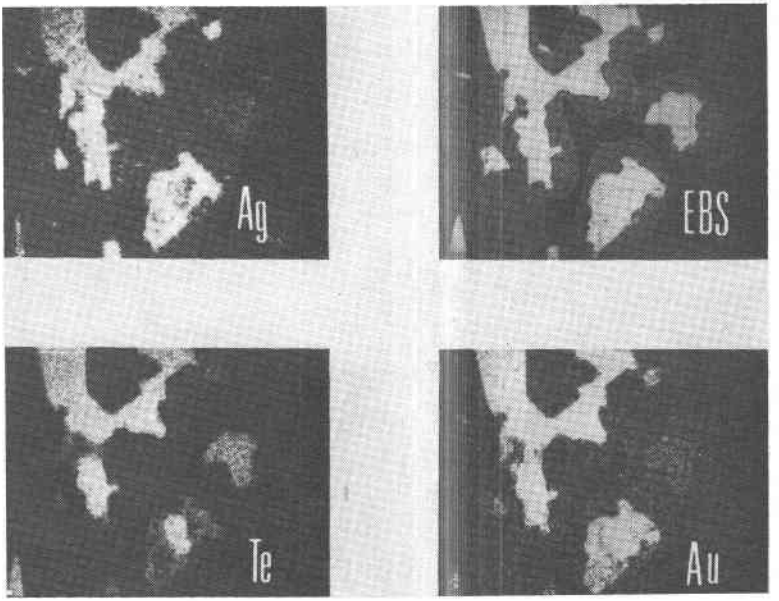

Fig. 1. Tellurides occupying the centers of euhedral pyrite. EBS=Back scattered electrons. White: phases containing elements of high atomic number. Grey: Pyrite Black: Gangue. X-ray scanning images show the distribution of Ag, Te and Au. Telluride in six-sided pyrite grain is coloradoite, HgTe (no Au or Ag) Emperor Mine, Vatukoula, Fiji Grid size magnification×100.

TABLE 1. ELECTRON PROBE MICROANALYSES OF SYLVANITE

Element	1	2	3	4	5	6	7	8
Au	24.19	31.4± .4	29.1± .4	27.5± .3	27.72	31.2± .3	26.1± .3	23.6± .3
Ag	13.22	6.6± .3	10.8± .2	11.7± .2	11.75	9.5± .2	11.6± .2	13.2± .2
Te	62.59	59.9± .4	59.6± .5	60.1± .4	60.32	59.8± .5	62.7± .6	61.7± .4
Total	100.00	97.9	99.5	99.3	99.79	100.5	100.4	98.5

1. $AuAgTe_4$. 2. Emperor Mine, Vatukoula, Fiji. (EFS65) 3. "Fiji Islands" (R) 4. Vatukoula, Fiji (R388) 5. Loloma, Fiji (Analysis by Edwards, in Stilwell 1949, p. 16) 6. Cripple Creek, Colorado (R436) 7. Inter Ocean Mine, Sunshine, Boulder Co., Colorado (JL3046) 8. Red Cloud Mine, Boulder, Colorado (R267).

Abbreviations in this and subsequent tables: R = Peacock collection, University of Toronto; JL = Johnson-Lewis collection, University College London (England); M = Royal Ontario Museum; EFS = collected by the author.

tion from the latter locality. The frequent occurrence of tellurides in the centers of pyrite crystals is of significance for aspects of ore genesis and ore dressing and has not been illustrated so far.

The sylvanites investigated by microprobe analysis (Table 1) did not reveal compositional variations within single crystals. The Emperor Mine sylvanites (Table 1) are comparatively poor in silver: 6–10 percent, as compared to 13.22 percent for $AuAgTe_4$. They show, in fact, the lowest Ag-contents analysed or recorded in the literature for natural sylvanites. Cabri (1965) investigated synthetic sylvanites within the range 6.7–12 percent, at temperatures ranging from 270° to 350°C by X-ray methods and stated that the minimum Ag-content of natural sylvanites reported so far is 9.18 percent. Au/Ag-ratios of sylvanites are no doubt influenced by the supply of the respective elements and by the temperature of formation. In case microscopic evidence suggests equilibrium conditions, analysed telluride assemblages may be used as geological thermometers. It has, for instance, been possible to determine the temperature of formation of a sylvanite-stützite assemblage from the Red Cloud Mine, Boulder, Colorado, as about 230°C (Stumpfl and Rucklidge, 1968). No attempt has been made to interpret the coexistence of sylvanite with petzite in the Emperor ores in the light of equilibrium conditions: There is microscopic evidence suggesting that the two phases have been emplaced at separate stages of mineralisation, petzite and coloradoite replacing sylvanite.

Spectral reflectivity data on sylvanites are summarized in Table 2. Three essential aspects emerge from this tabulation:

a) Au-rich sylvanite gives higher reflectivity values than stoichiometric sylvanite.
b) The increase is more pronounced for R_α, than for R_γ. This means lower bireflectance for Au-rich sylvanites.

TABLE 2. SPECTRAL REFLECTIVITY OF SYLVANITE

Wavelength nm	Emperor Mine, Vatukoula, Fiji (31.4% Au, 6.6% Ag)		Red Cloud Mine, Boulder Co. Colorado (23.6% Au, 13.2% Ag)	
	R_a, %	R_γ, %	R_a, %	R_γ, %
440	42.0	56.3	39.0	57.0
460	44.6	57.5	40.1	57.4
480	47.0	59.1	41.4	58.1
500	48.4	60.6	43.1	58.8
546	50.8	61.2	44.2	59.3
589	50.0	59.5	43.0	58.4
600	51.5	61.1	44.1	58.6
620	52.3	61.6	45.2	59.2

c) The differences are more pronounced at medium and higher wavelengths, *i.e.* 500–600 nm.

Bowie and Taylor give reflectivity values of 48–60 percent (1958). Even though their measurements were performed in white light, the high value for R_a, is similar to that of nonstoichiometric Vatukoula sylvanite. This observation might serve to exemplify the significance of coordinated reflectivity and electron probe measurements for establishing a meaningful system of quantitative optical parameters. Kelly and Goddard (1969) give values of 44–57 percent in "white light" (2850°K) and 47.0–61.8 percent at 586 nm.

Calaverite and Krennerite. The independent character of, and the lack of polymorphic relationships between, these two minerals has been established by Cabri (1965) and by Cabri and Rucklidge (1968). Calaverite is $AuTe_2$; Krennerite has the approximate formula Au_4AgTe_{10} or, simplified, $(Au, Ag)Te_2$. The specimens investigated show a considerable degree of optical and chemical homogeneity. No variations of composition were detected in single grains. Minor differences only appear to

TABLE 3. ELECTRON PROBE MICROANALYSES OF CALAVERITE AND KRENNERITE

	1	2	3	4	5	6	7	8
Au	43.56	41.3 ± .9	42.1 ± 1.1	39.7 ± .4	43.9 ± 1.1	42.4 ± .6	36.1 ± .8	36.8 ± 1.2
Ag	—	1.03 ± .16	0.43 ± .08	1.49 ± .02	.86 ± .03	0.7 ± .02	4.85 ± .08	3.3 ± 1.8
Te	56.44	56.9 ± .4	56.2 ± .3	57.7 ± .3	57.2 ± .4	57.2 ± .3	58.8 ± .2	57.6 ± .5
Total	100.00	99.2	98.7	98.9	101.9	100.3	99.7(5)	97.7

1. $AuTe_2$ Nos. 2–6 are calaverite analyses, 7–8 krennerite. 2. Cripple Creek, Colorado (R437). 3. Wright Hargreaves Mine, Kirkland Lake, Ontario (EFS997). 4. Kalgoorlie, W. A. (R296). 5. Benguet Mine, Philippines (R356B). 6. Tough Oakes Mine, Kirkland Lake, Ontario (M13536) 7. Krennerite, Kalgoorlie, W. A. (R294). 8. Krennerite, Emperor Mine, Vatukuola, Fiji (EFS1140).

exist between calaverites from different deposits. Cabri and Rucklidge (1968) report the occurrence of 0.3 percent Cu and 0.77 percent Sb in one calaverite, and 0.6 percent Cu in one krennerite. Traces of these elements were not detected in the tellurides listed in Tables 1 and 3.

Silver is present in all the calaverites analysed (Table 3), but in smaller amounts in Kirkland Lake material. The Benguet calaverite is associated with native gold, the Ag-content of which has been determined by micro-

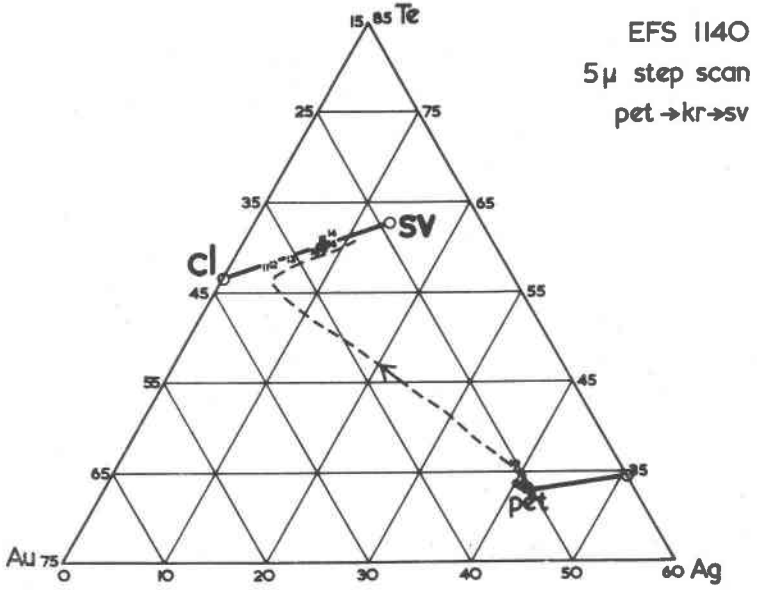

FIG. 2. Step scan (5 micron intervals) across a petzite—krennerite—sylvanite interface. Arrow indicates direction of scan. Emperor Mine, Vatukoula, Fiji.

probe to be in the range of 11–12 percent. Markham (1960, p. 1463) concludes that the assemblage calaverite—gold is "quite rare". He states that hessite, petzite and calaverite are not necessarily in equilibrium with a pure gold phase, but rather with gold containing variable amounts of silver. The data obtained on the Benguet paragenesis seem to support this view.

The results obtained agree with Cabri's (1965) phase diagram, which indicates a maximum silver content of 2.8 ± 0.2 percent in calaverites. A step scan across a petzite—krennerite—sylvanite interface (Fig. 2) reveals a certain compositional gradient on the kr—sv line. This is proposed to be due to diffusion processes rather than to a spread of the com-

TABLE 4. REFLECTIVITIES OF CALAVERITE AND KRENNERITE

Mineral	Cameron 1961	Kelly and Goddard 1969 "White light"	586 nm
Calaverite	63.2	52.1–59.5	56.2–66.2
Krennerite	60.9	49.9–58.5	51.5–61.5

positional field. All analyses of separate krennerite grains from the Emperor Mine occupy a well-defined area. Considering the low temperature of formation of telluride assemblages, moderate heating in young volcanic environments such as Vatukoula might well facilitate diffusion on a microscale.

Optically calaverite and krennerite are very similar; determinations based on optical evidence only may be doubtful. Data on spectral reflectivity of these two minerals have not been obtained so far. Available reflectivity values for white and yellow light are summarized in Table 4. Separation of krennerite or calaverite for X-ray diffraction was not possible because of extremely fine-grained intergrowths. Electron probe analysis thus represents a reliable diagnostic method.

Nagyagite. Nagyagite from Nagyag, and from Cripple Creek, Colorado, was analysed in the course of this study (Table 5). In the latter locality, it forms zones around large sylvanite crystals, and is itself surrounded by seems of altaite. This suggests increasing lead content of the ore-forming solutions with decreasing temperature of formation. Nagyagite from the type locality is found as large crystals, more than one millimetre in size.

TABLE 5. ELECTRON PROBE MICROANALYSES OF NAGYAGITE

Element	1	2	3
Pb	57.16	57.6± .3	58.8 ± .3
Au	7.41	7.6± .2	9.0 ± .2
Ag	—	—	0.17± .05
Te	17.87	16.4± .2	15.1 ± .2
Sb	6.99	7.4± .1	7.8 ± .1
S	10.33	10.0± .1	10.1 ± .1
Total	100.08	99.0	101.0

1. Nagyag, Transsylvania, Average of two analyses (Dana, 7th ed., p. 168), includes 0.32 Fe.
2. Nagyag (R370) 3.
3. Cripple Creek, Colorado (R436).

Electron probe traverses across several nagyagite crystals revealed remarkable homogeneity: No variations in composition could be observed in single grains. The agreement between a "classical" chemical analysis and electron probe analysis of Nagyag material (Table 5) is remarkable. Cripple Creek nagyagite contains slightly more gold. The formula widely used in the literature is $Pb_5Au(Te,Sb)_4S_{5-8}$. It would, however, appear more appropriate to group S and Te together; accordingly, the nagyagites analysed by electron probe correspond to the formulae $Pb_5Au_{0.66}Sb_{1.06}(Te_{2.23}S_{5.40})_{7.63}$ (Nagyag) and $Pb_5Au_{0.77}Sb_{1.10}(Te_{2.02}S_{5.43})_{7.45}$ (Cripple Creek). It is interesting to note the lack of compositional variations in this complex telluride.

Acknowledgements

Part of the results discussed in this note was obtained while the author was Visiting Professor at the University of Toronto. Thanks are due to Prof. E. W. Nuffield, Prof. J. C. Rucklidge and Dr. J. Mandarino for the loan of specimens and for stimulating discussions, and to Mr. S. Suensilpong for assistance with the optical measurements. Dr. L. Cabri kindly made available a set of synthetic telluride standards. His constructive criticism of the manuscript is much appreciated.

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Manuscript received, July 7, 1969; accepted for publication, January 17, 1970.